

*Acknowledgements*

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## PRELIMINARY NOTES

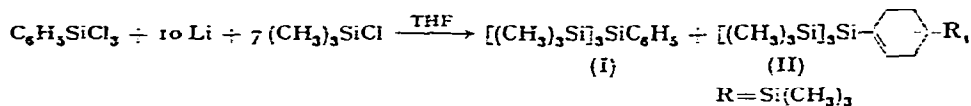
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### Synthesis of some pentasilyl-substituted cyclohexenes

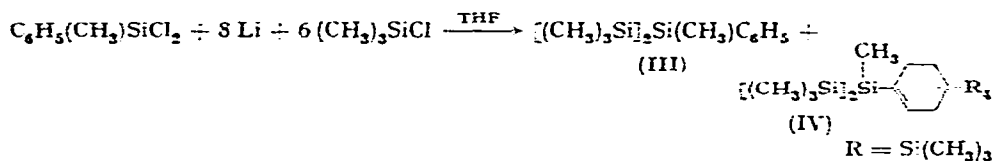
Earlier reports from these Laboratories<sup>1-3</sup> have shown that the reaction of certain chlorosilanes with lithium and chlorotrimethylsilane in tetrahydrofuran (THF) is a convenient method for a one-step preparation of some trimethylsilyl-substituted silanes. By this procedure, silicon tetrachloride gave high yields of tetrakis(trimethylsilyl)silane<sup>1</sup>. Methyltrichlorosilane<sup>2</sup>, dimethyldichlorosilane and methylethyldichlorosilane<sup>3</sup> afford very good yields of tris(trimethylsilyl)methylsilane, octamethyltrisilane and 2-ethylheptamethyltrisilane, respectively.

As a result of studies designed to determine the scope of this *in situ* type reaction, we are now reporting that phenyl-substituted chlorosilanes react with lithium and chlorotrimethylsilane to give, in addition to the normal coupling products, pentasilyl-substituted cyclohexenes. Thus, phenyltrichlorosilane gave the known<sup>4</sup> tris(trimethylsilyl)phenylsilane (I) and 2-[(tetra(trimethylsilyl)cyclohexen-1-yl]-2-trimethylsilylhexamethyltrisilane (II), m.p. 222-227°. (Found: mol. wt., 617.  $\text{C}_{27}\text{H}_{63}\text{Si}_5$ . Calcd.: mol. wt., 617.5.)

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Similarly, phenylmethyldichlorosilane gave the previously described<sup>4,5</sup> 2-phenylheptamethyltrisilane (III) and 2-[tetra(trimethylsilyl)cyclohexen-1-yl]heptamethyltrisilane (IV), m.p. 120–121°. (Found: mol. wt., 558. C<sub>25</sub>H<sub>62</sub>Si<sub>7</sub>. Calcd.: mol. wt., 559.)



The NMR spectrum of IV, (in carbon tetrachloride) relative to TMS standard, shows a doublet assigned to the olefinic proton, centered at 5.88 ppm ( $J = 5$  cps), and a multiplet (2.1–1.1 ppm) for the four aliphatic protons. Expansion of the methyl region (50 cycles) exhibited, in addition to a single methyl group, five different trimethylsilyl groups in a ratio of 2:1:1:1:1. Additional support for the assigned structure was afforded by IR, UV and mass spectral studies. Similarly, the structure of II was assigned on the basis of data obtained by these techniques. The exact positions of the trimethylsilyl groups on the ring have not been determined. However, it is believed that one of these groups is on each of the four aliphatic carbons. Such a structure could result from direct coupling of a radical anion or dianion, formed by transfer of one or more electrons to the benzene ring, with chlorotrimethylsilane. Any other distribution of four trimethylsilyl groups on the aliphatic carbons of the ring would necessitate hydrogen transfer.

Our reaction conditions are similar to those used by Weyenberg and Toporcer<sup>6</sup> in the synthesis of 3,6-disilyl-1,4-cyclohexadienes. These workers proposed a mechanism which involves the coupling of chlorosilanes and anion radicals<sup>6,7,10</sup>. However, our results differ from theirs in that a greater degree of reduction occurred\*. A closer analogy appears to be the reaction of biphenyl with sodium and chlorotrimethylsilane in tetrahydrofuran to give phenyltetra(trimethylsilyl)cyclohexene<sup>8</sup>.

A few preliminary reactions gave the normal coupling products (I and III) in yields that ranged from 0 to 25%; however, compound (II) has been isolated in as high as 75% yield. Further research is being conducted to establish the course of this reaction and to determine if the reduction reaction is applicable to other substituted types.

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\* The degree of reduction obtained in the work reported here is similar to that obtained by Benkeser *et al.* in the reaction of aromatic compounds with lithium and amines<sup>9</sup>.

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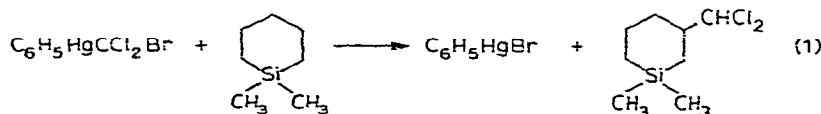
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### **CCl<sub>2</sub> insertion into tetraalkyl-silicon and -tin compounds via phenyl (bromodichloromethyl)mercury**

Recent studies have shown that CCl<sub>2</sub> insertion into benzylic C-H bonds of phenylalkanes can be effected with sodium trichloroacetate in 1,2-dimethoxyethane<sup>1</sup>, or, in better yield, with phenyl(bromodichloromethyl)mercury<sup>2</sup>. Use of the latter reagent even made possible the preparation of (dichloromethyl)cyclohexane from cyclohexane in 32% yield<sup>2</sup>.

In a continuation of these studies we report here concerning surprisingly specific CCl<sub>2</sub> insertions into β C-H linkages of sila- and stanna-cyclohexanes and of the *n*-propyltrimethyl derivatives of silicon and tin. For example, when a solution of 0.03 mole of 1,1-dimethyl-1-silacyclohexane and 0.01 mole of phenyl(bromodichloromethyl)mercury in 20 ml of benzene was heated at reflux for 2 h, phenylmercuric bromide precipitated (92%), and fractional distillation gave as sole organosilicon product 3-dichloromethyl-1,1-dimethyl-1-silacyclohexane in 68% yield (eqn. 1). The product had a satisfactory combustion analysis; it was characterized by b.p. 81° (6 mm), *n*<sub>D</sub><sup>25</sup> 1.4878. Its NMR spectrum (CCl<sub>4</sub>) showed a doublet (*J* = 3.5 c.p.s.) at 5.71 p.p.m. (1H), singlet at 0.07 p.p.m. (6H) and complex absorption (9H) in the region 0.3-2.1 p.p.m. downfield from TMS. The mass spectrum was consistent with this



structure. An unambiguous structure proof for this product was given by its reduction with sodium in liquid ammonia to 1,1,3-trimethyl-1-silacyclohexane, which was identical in all respects with authentic material prepared by reaction of the di-Grignard reagent from 1,5-dibromo-2-methylpentane with silicon tetrachloride, followed by methylation with methylmagnesium bromide.

A similar reaction of phenyl(bromodichloromethyl)mercury with *n*-propyltrimethylsilane gave  $\gamma,\gamma$ -dichloroisobutyltrimethylsilane, *n*<sub>D</sub><sup>25</sup> 1.4561, but only in 15% yield. Its NMR spectrum unambiguously defined its structure as (CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>-